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Paper

Design of New Mesostructured Material: Vanadate–Poly(Ethylene Glycol) Composite

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新奇メソ構造材料（バナジン酸－ポリエチレングリコール複合体）の設計

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A new method for designing nanomodified inorganic–organic materials is proposed, and one example of synthesizing mesostructured vanadate–poly(ethylene glycol) composite is demonstrated. Commercially available poly (ethylene glycol) was changed in its terminal hydroxy group(s) to ammonium head group by two-step sequential tosylation/nucleophilic substitution in order to enable connection with the vanadate framework component. Self-organization of vanadate and the new organic template was successfully processed in the aqueous mixture to precipitate as a composite by adding sodium chloride. We discuss not only the design of a mesostructured material, but also the reasonable treatment for obtaining it from the mixture by the same technique as the volume shrinkage of an amphiphilic block copolymer in water. [Received July 14, 2003; Accepted September 30, 2003]

Key-words: *Self-organization, Exchange of functional group, Tosylation, Nucleophilic substitution, Vanadate, Volume shrinkage, Amphiphilic block co-polymer*

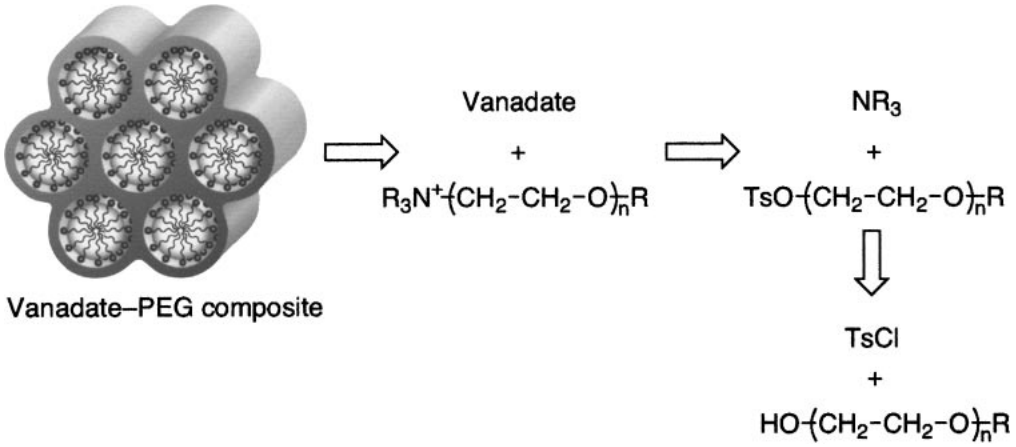
1. Introduction

Self-organization process that gives mesoporous inorganics especially in the case of the silica-surfactant systems has been used for various engineering applications such as catalytic, wave-guide, and low-k materials,[1)–3)] since the MCM family was developed by Beck et al.[4)] However, it is thought that general mesoporous metal oxides cannot be synthesized, with the exception of two systems: one is mesoporous silica,[4)] and the other is the combination of block copolymers and metal oxide precursors.[5)] We report here one method for preparing a mesostructured vanadate-organic composite that in a way corresponds to mesoporous vanadium oxide.

Mesoporous metal oxides have not been synthesized using the usual combination of inorganic and ionic surfactant template systems, because it shows mesostructural deformation during the process of removing the organic template component. Luca et al. reported that vanadate-hexadecyltrimethylammonium (C_{16}TMA) composite deforms in its mesostructure within a calcination process.[6)] In addition, Zhou and Honma examined a low-temperature calcination (at 160°C) of a vanadate-C_{16}TMA thin film, and observed a phase transformation in its mesostructure during the heat treatment.[7)] The deformation of the mesostructure has also been reported to occur during the calcination of germanium sulfide mesostructured materials,[8)] and it therefore should be recognized as a common problem for preparation of mesoporous inorganic materials, except for mesoporous silica. In the previous work, we investigated, in detail, the mesostructural change in vanadate-C_{16}TMA composite, and found that the mesostructure of the composite varies at a process of controlling the surfactant concentration (calcination and solvent extraction) as follows: lamellar > cubic (*Ia*3*d*) > two-dimensional monoclinic (*p*2) > hexagonal (*p*6*m*), where the sequence is in the order of the concentration of the surfactant component against the vanadate framework.[9),10)] Our discussion covered its reason that consists of the difference between vanadate-C_{16}TMA and silica-C_{16}TMA systems. We believe that the mesostructural transformation occurs in the vanadate-C_{16}TMA system because of the strong ionic character of the vanadate framework and its surroundings. In contrast for the silica-C_{16}TMA system, the mesostructure remains unchanged from the as-prepared composite to the final porous product, because the silica framework has weaker ionic character by comparison. The strong ionic character of the vanadate framework causes strong interfacial tension between the framework and the head group of the surfactant molecule to result in the mesophase transformation and deformation during the calcination or solvent extraction, while the weak ionic character of the silica framework does not enough.

If a mesoporous vanadium oxide were synthesized, it could be applied to cathode materials of lithium ion batteries and electrochemical capacitors.[11)] In these imaginary applications, the material would be used with electrolyte (e.g., 4-methyl-[1,3]dioxolan-2-one) which occupied in the mesopore beforehand. However, a designed mesostructured vanadate-organic composite that contains an electrolyte component is expected to yield the same result in the purpose of electrochemical applications. Therefore, we tried to synthesize a new template and a new vanadate-template composite. In this paper, we explain how to design the new template material that contains an electrolyte component, and how to synthesize the new vanadate-template composite. The purpose is to show our concept of designing nanomodified materials by demonstrating one example of the inorganic-organic composite.

At first, we made an antithetic plan for the new composite, and that we selected is shown in **Scheme 1**. The new template needs to have both of ammonium head group (in order to bond chemically with vanadate ion or framework) and poly(oxy-ethylene) unit (in order to work as an electrolyte) in one molecule. The terminal ammonium head group of the template material shown in this scheme can be created by two-step exchange of the hydroxy group: sequential tosylation/nucleophilic substitution.[12)] Therefore, commercially available poly(ethylene glycol) was selected as the starting material to obtain the target chemical. We examined to synthesize the poly(ethylene glycol) terminated with ammonium tosylate (PEG–TWAT) and the mesostructured vanadate-PEG



Scheme 1. Antithesitic diagram for the vanadate-PEG composite. The letter *R* indicates the alkyl group or hydrogen atom, and Ts indicates the 4-methyl-benzenesulfonyl (tosyl) group. The closed circles, the wavy lines, and the surrounding solid wall in the illustration on the left side of this scheme represent ammonium head groups, PEG skeletons, and the vanadate framework, respectively.

composite on the basis of the antithetic route.

2. Results and discussion

2.1 Synthesis of PEG–TWAT

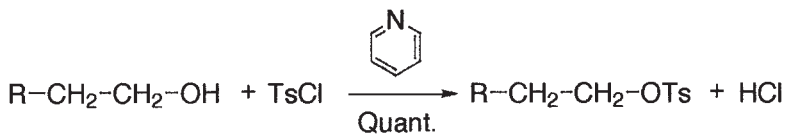
Two types of commercially available PEG were chosen as the starting materials for synthesizing PEG–TWAT: 2-[2-(2-butoxy-ethoxy)-ethoxy]-ethanol (PEG1), and PEG of *Mw* ca. 600 (PEG2). We applied the sequential tosylation/nucleophilic substitution (Scheme 1) to them, because both of these reactions are never expected to occur in less than 99% yield.

The tosylation of the hydroxy group in PEG1 was carried out at ice-bath temperature in pyridine to trap hydrochloric acid of the subproduct, as shown in **Scheme 2**. In order to check for the existence of the starting material (the hydroxy group) during the reaction as well as during the purification of a silica gel chromatography, reduction of manganese was used as a color reaction, i.e., an alkaline solution of potassium permanganate(1-) was used as a color reagent. This reaction gives the product of 2-[2-(2-butoxy-ethoxy)-ethoxy]-ethyl 4-methyl-benzenesulfonate (PEG–Ts1) in quantitative yield. The substitution of the terminal tosylate ester portion in PEG–Ts1 by triethylamine was carried out at the reflux temperature of ethanol, as shown in **Scheme 3**. The point of this reaction is to add the nucleophile in excess (at least 1.2 equivalents against one ester portion). The nucleophilic substitution also gives the product of {2-[2-(2-butoxy-ethoxy)-ethoxy]-ethyl}-triethyl-ammonium 4-methyl-benzenesulfonate (PEG–TWAT1) in quantitative yield. The above preparation was applied to the other starting material, PEG2, and gives both PEG–Ts2 and PEG–TWAT2 in quantitative yields.

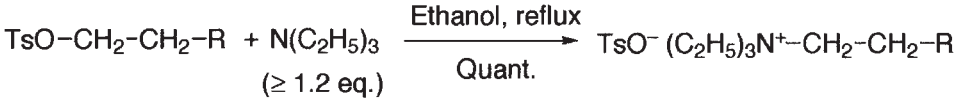
2.2 Self-organization of vanadate and new template

An aqueous vanadate solution (V^{5+} 0.2 mol/l, pH 4.3) was first prepared in almost the same manner as the experimental method described in the previous paper,[9),10)] and we tried to use it in the self-organizing reaction with the above templates. Even after mixing the vanadate solution and the template material (PEG–TWAT1 or PEG–TWAT2), no precipitate was observed in the mixture, because the template contains a hydrophilic PEG skeleton and this results in high solubility of the vanadate-PEG couple in water. Some manipulation was needed to apply to the mixture solution in order to precipitate it as a composite.

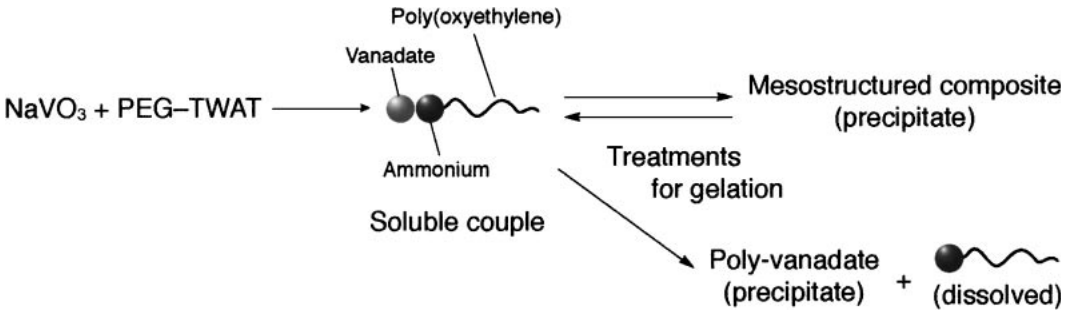
In the theory of polymer solution, a hydrogel (e.g., poly-acrylamide gel) containing water shrinks in volume when some energy is applied to the system.[13)] This is due to the loss of affinity between water molecules and the polymer; the same principal is applied to nonionic amphiphilic polymers (e.g., poly(ethylene oxide)-poly(propylene oxide) block copolymer).[14)–16)] Effective operations for disconnecting water molecules from the polymer are increasing the temperature, controlling the pH, varying the solvents combination, and increasing the salt concentration. These treatments might be applicable to the vanadate-PEG system in order to give a precipitate of its composite, because the couple contains a hydrophilic PEG skeleton binding with a hydrophobic part (vanadate and ammonium head group, both of which lose their ionic characters, i.e., solubility, after charge matching), and it



Scheme 2. Tosylation of the terminal hydroxy group in PEG1. The letters *R* and Ts indicates the 2-(2-butoxy-ethoxy)-ethoxy group and tosyl group, respectively.



Scheme 3. Nucleophilic substitution of the terminal tosylate ester portion in PEG–Ts1 to triethyl- ammonium head group. The letters *R* and Ts indicates the 2-(2-butoxy-ethoxy)-ethoxy group and tosyl group, respectively.



Scheme 4. Possible mechanism for the formation of vanadate-PEG composite and for the precipitation of poly-vanadate.

can be considered as an amphiphilic polymers. However, all of them may also yield yellow or brown precipitates of vanadate alone (i.e. forming poly-vanadate) at the same time, as shown in **Scheme 4**. We examined the above operations (i.e. heating of the mixture solution, adding propan-2-one or acetone to the solution, controlling the pH, and adding sodium chloride to it), and found that all the methods are possible to result in the formation of poly-vanadate. We also found that there is a time lag between the precipitation of poly-vanadate and that of vanadate-PEG composite, i.e., the precipitation rate of the composite is faster than that of poly-vanadate, when the vanadate-PEG composite is formed in these systems.

The time lag was successfully used only in the case of the adding sodium chloride to the mixture of vanadate and the PEG–TWAT template. In the cases of the other operations, the poly-vanadate was formed, and it shows a low-angle powder X-ray diffraction (XRD) pattern of **Fig. 1** (a). When sodium chloride was added to the mixture containing PEG–TWAT2, the precipitate exhibited the XRD pattern shown in Fig. 1 (b). It consists of layered compound with the period of 1.8 nm, according to two XRD peaks at 4.9 and 9.7°, and the compound is speculated to be either a lamellae-like structured composite,[9),10)] or poly-vanadate containing water molecules in its layer structure.[17)] In both cases, the small *d*-space of the precipitate material does not fit in the category of mesostructured composites. When sodium chloride was added to the mixture containing PEG–TWAT1, the precipitate exhibits the XRD pattern in Fig. 1 (c). It consists of almost a single phase of a mesostructured composite (probably with a cubic structure, $Pm\bar{3}m$ with lattice parameter $a = 5.81$ nm). The indexes of its XRD peaks are shown in the same figure. We sometimes obtained poly-vanadate in the case of using both PEG–TWAT1 and PEG–TWAT2 templates. This case is that either sodium chloride was added in excess to the mixture (until it was saturated), or the mixture was left standing for a long time (until poly-vanadate was sufficiently formed). It is speculated that excess sodium chloride accelerates the formation of poly-vanadate, and that its formation is more stable than the formation of the vanadate-PEG composite.

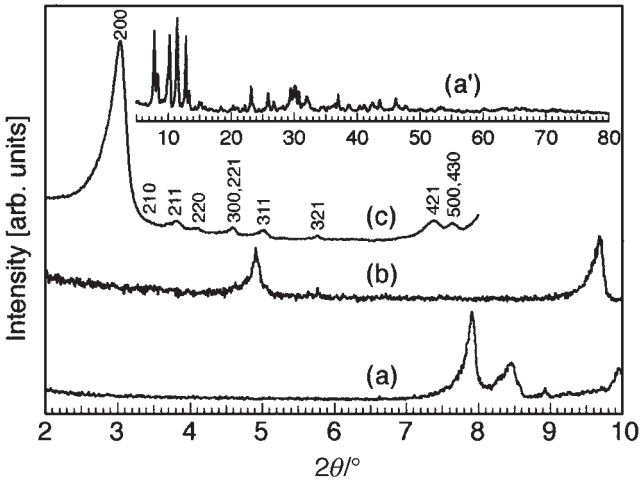


Fig. 1. XRD patterns of the precipitates after trying the self-organizing reactions. (a) This pattern was observed in the case of operations other than adding sodium chloride. The high-angle XRD pattern is shown in (a′). (b) This pattern was observed in the case of using PEG–TWAT2 template and adding sodium chloride. (c) This pattern was observed in the case of using PEG–TWAT1 template and adding sodium chloride.

The same speculation is applicable to the cases in which no vanadate-PEG composite was obtained using the other techniques (heating, adding acetone, and controlling pH). The operation of heating the mixture needed a long time to give a precipitate (for 2 d at 80°C, or for 4 d at 60°C), and therefore the poly-vanadate was sufficiently formed as a precipitate. The operations of adding acetone and controlling pH (adding hydrochloric acid) are believed to accelerate the formation of poly-vanadate much more than that of the vanadate-PEG composite, in the same manner as adding excess sodium chloride to the mixture. Thus, we concluded that the mesostructured vanadate-PEG composite can be obtained only under kinetically advantageous conditions in this system, and that poly-vanadate is, in contrast, thermodynamically stable to precipitate at most of the above treatments.

On the basis of the above discussion and results presented in the previous paper, we propose a new concept for designing a nano-modified inorganic–organic composite material. First, we should select an organic template and inorganic framework on the basis of the application of the nano-composite. In this study, a template of poly(ethylene glycol) terminated with ammonium tosylate and a vanadate framework were selected, because we would prepare a cathode material containing an electrolyte component for a lithium ion battery. It must be noted that the organic template material should have a portion that allows it to be connected with inorganic framework (e.g., ammonium head group in our system). Sometimes the required template must be synthesized because it is not commercially available. PEG–TWAT was efficiently prepared in this study by the rudimentary methods. Finally, the organic template and the inorganic framework materials should bond with each other under a self-organizing reaction in a solvent to be precipitated as a mesostructured composite. An important thing is that a suitable reaction should be carried out for the composite. In the present example, we concluded that the treatment of adding sodium chloride (i.e., increasing the salt concentration) must be selected to obtain the vanadate-PEG composite and to keep down the byproduct of poly-vanadate.

3. Conclusion

We synthesized a new template for a self-organization process, and designed a new vanadate-organic template composite for the

cathode material of a lithium ion battery. The template material, poly(ethylene glycol) terminated with ammonium tosylate, was prepared by two-step exchange of terminal hydroxy group(s) of poly(ethylene glycol) in net quantitative yield. The composite was synthesized by self-organization of vanadate and the new template, and was precipitated upon adding sodium chloride, which is essentially the same technique as that upon which amphiphilic polymer shrinks in volume in water through the loss of affinity between water molecules and the polymer. We demonstrated an example of the new method for designing nanomodified materials. In subsequent study, we will estimate the electrochemical property of the new composite useed as a cathode material, as well as synthesize various organic template materials and various functional mesostructured composites.

4. Experimentals

Nuclear magnetic resonance (NMR) and infrared (IR) spectra were recorded using JEOL LA–500 and PerkinElmer 1640 spectrometers, respectively. The symbols of s, d, t, q, m, TMS, *s*, *m*, *w* in the following spectral data mean singlet, doublet, triplet, quartet, multiplet, tetramethylsilane, strong, medium, and weak, respectively. The "δ" and "J" values in the following NMR data are the chemical shift and the coupling constant, respectively. X-ray diffraction (XRD) patterns were measured using a Rigaku RINT-2500V diffractometer with Cu Kα radiation.

2-[2-(2-Butoxy-ethoxy)-ethoxy]-ethyl 4-methyl-benzenesulfonate (PEG–Ts1)

First, 206 mg of 2-[2-(2-butoxy-ethoxy)-ethoxy]-ethanol (PEG1) was dissolved in 1 ml of pyridine at ice-bath temperature. Separately, 229 mg of 4-methyl-benzenesulfonyl chloride (TsCl) was dissolved in 1 ml of pyridine at room temperature. To the PEG1 solution in an ice bath, the TsCl solution was added through a canula, and the resultant mixture was stirred at ice bath temperature for 1 h, and then at room temperature for 1 h. The reaction was quenched by diluting with ethyl acetate, and the mixture was filtered through a silica gel pad. The filtrate was concentrated in vacuo, and then the product was purified by silica gel chromatography. Yield: 360 mg (> 99%). CHN elemental analysis (perfectly purified product should be composed of C 56.6%, H 7.8%, N 0%): C 56.2%, H 7.4%, N <0.1%. Ion chromatography after flask calcination (perfectly purified product should be composed of N 0%, S 8.9%): N <0.01%, S 7.9%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS standard) δ [ppm] 0.91 (t, $J = 7.6$ Hz, 3H), 1.36 (tq, $J = 8.0$, 7.6 Hz, 2H), 1.57 (tt, $J = 8.0$, 6.6 Hz, 2H), 2.78 (s, 3H), 3.45 (t, $J = 6.6$ Hz, 2H), 3.54–3.70 (m, 8H), 3.69 (t, $J = 4.8$ Hz, 2H), 4.16 (t, $J = 4.8$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.80 (d, $J = 8.0$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ [ppm] 13.93, 19.26, 21.63, 31.67, 68.59, 69.19, 69.96, 70.41, 70.59, 70.68, 71.12, 127.83, 129.67, 132.83, 144.62. IR (neat) 2957 (*m*), 2931 (*m*), 2870 (*m*), 1598 (*w*), 1455 (*w*), 1360 (*s*), 1178 (*s*), 1120 (*s*), 817 (*m*) cm^{-1}.

{2-[2-(2-Butoxy-ethoxy)-ethoxy]-ethyl}-triethyl-ammonium 4-methyl-benzenesulfonate (PEG–TWAT1)

First, 3.60 g of 2-[2-(2-butoxy-ethoxy)-ethoxy]-ethyl 4-methyl-benzenesulfonate was dissolved in 15 ml of ethanol. To this solution, excess triethylamine (at least 1.7 ml) was added, and the mixture was refluxed for 12 h. After completion of the reaction was confitmed by thin layer chromatography (TLC), the product was purified by concentrating in vacuo. Yield: 4.61 g (> 99%). CHN elemental analysis (perfectly purified product should be composed of C 59.8%, H 9.4%, N 3.0%): C 56.9%, H 8.9%, N 2.8%. Ion chromatography after flask calcination (perfectly purified product should be composed of N 3.0%, S 7.0%): N 0.1%, S 6.2%. ^{1}H NMR (400 MHz, CD_3OD, TMS standard) δ [ppm] 0.92 (t, $J = 7.2$ Hz, 3H), 1.23 (t, $J = 7.4$ Hz, 9H), 1.38 (tq, $J = 8.4$, 7.2 Hz, 2H), 1.53 (tt, $J = 8.4$, 6.4 Hz, 2H), 2.36 (s, 3H), 3.34 (q, $J = 7.4$ Hz, 6H), 3.40–3.65 (m, 12H), 3.67–3.82 (m, 2H), 7.24 (d, $J = 8.0$ Hz, 2H), 7.70 (d, $J = 8.0$ Hz, 2H). ^{13}C NMR (100 MHz,CD_3OD) δ [ppm] 7.87, 14.32, 20.29, 21.37, 32.82, 49.64, 54.64, 57.54, 65.22, 71.09, 71.26, 71.36, 71.40, 71.44, 71.88, 126.82, 129.67, 141.29, 143.92. IR (neat) 2956 (*m*), 2932 (*m*), 2870 (*m*), 1642 (*w*), 1458 (*m*), 1204 (*s*), 1191 (*s*), 1122 (*s*), 820 (*m*) cm^{-1}.

Poly(ethylene glycol) terminated with 4-methyl-benzenesulfonyl groups (PEG–Ts2)

PEG–Ts2 was prepared from PEG (*Mw* ca. 600) in the same manner as the preparation of 2-[2-(2-butoxy-ethoxy)-ethoxy]-ethyl 4-methyl-benzenesulfonate. CHN elemental analysis (perfectly purified product should be composed of C 53.1%, H 8.0%, N 0%): C 52.4%, H 7.0%, N <0.1%. Ion chromatography after flask calcination (perfectly purified product should be composed of N 0%, S 7.0%): N <0.01%, S 6.6%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS standard) δ [ppm] 2.45 (s, 6H), 3.52–3.73 (m, 52H), 4.17 (t, $J = 4.2$ Hz, 4H), 7.35 (d, $J = 8.0$ Hz, 4H), 7.80 (d, $J = 8.0$ Hz, 4H). ^{13}C NMR (100 MHz,CD_3OD) δ [ppm] 21.58, 68.51, 69.18, 70.35, 70.40, 70.43, 70.44, 70.49, 70.57, 127.74, 129.65, 132.76, 144.60. IR (neat) 2905 (*m*), 2870 (*m*), 1598 (*w*), 1454 (*w*), 1355 (*s*), 1177 (*s*), 1119 (*s*), 818 (*m*) cm^{-1}.

Poly(ethylene glycol) terminated with triethylammonium 4-methyl-benzenesulfonate (PEG–TWAT2)

PEG–TWAT2 was prepared in the same manner as the preparation of 2-[2-(2-butoxy-ethoxy)-ethoxy]-ethyl 4-methyl-benzenesulfonate. CHN elemental analysis (perfectly purified product should be composed of C 56.4%, H 9.3%, N 2.5%): C 53.6%, H 7.9%, N 2.4%. Ion chromatography after flask calcination (perfectly purified product should be composed of N 2.5%, S 5.8%): N 0.08%, S 5.2%. ^{1}H NMR (400 MHz, CD_3OD, TMS standard) δ [ppm] 1.25 (t, $J = 7.6$ Hz, 18H), 2.37 (s, 6H), 3.38 (q, $J = 7.6$ Hz, 12H), 3.34–3.67 (m, 44H), 3.82–3.88 (m, 4H), 7.24 (d, $J = 8.0$ Hz, 4H), 7.70 (d, $J = 8.0$ Hz, 4H). ^{13}C NMR (100 MHz, CD_3OD) δ [ppm] 7.79, 21.29, 54.54, 57.42, 65.16, 71.17, 71.23, 71.31, 71.35, 71.39, 72.27, 126.73, 129.61, 141.28, 143.71. IR (neat) 2907 (*m*), 2871 (*m*), 1636 (*w*), 1458 (*m*), 1211 (*s*), 1196 (*s*), 1125 (*s*), 813 (*m*) cm^{-1}.

Vanadate-PEG composite

First, sodium metavanadate(1-) was dissolved in 10 ml of aqueous sodium hydroxide solution (1.0 mol/l). To this solution, hydrochloric acid and water were added in order to prepare 50 ml of vanadate solution (V^{5+} 0.2 mol/l, pH 4.3). {2-[2-(2-Butoxy-ethoxy)-ethoxy]-ethyl}-triethyl-ammonium 4-methyl-benzenesulfonate (4.61 g) was added to the vanadate solution, and the resultant mixture was stirred at room temperature for a few minutes. Sodium chloride was added to the mixture solution until the precipitation of vanadate-PEG composite was observed in the mixture (just before the saturation). The precipitate was filtered, and dried at 76°C for 14 h. Yield: 380 mg.

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